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Quantifying the importance of orbital over spin correlations in δ-Pu within density-functional theory

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Abstract

Spin and orbital electron correlations are known to be important when treating the high-temperature δ phase of plutonium within the framework of density-functional theory (DFT). One of the more successful attempts to model δ-Pu within this approach[1,2] has included condensed-matter generalizations of Hund's three rules for atoms, i.e, spin polarization, orbital polarization, and spin-orbit coupling. Here we perform a quantitative analysis of these interactions relative rank for the bonding and electronic structure in δ-Pu within the DFT model. The result is somewhat surprising in that spin-orbit coupling and orbital polarization are far more important than spin polarization for a realistic description of δ-Pu. We show that these orbital correlations on their own, with out any formation of magnetic spin moments, can account for the low atomic density of the δ phase with a reasonable equation-of-state. In addition, this unambiguously non-magnetic (NM) treatment produces a one-electron spectra with resonances close to the Fermi level consistent with experimental valence band photoemission spectra.

PACS numbers: 71.15.Mb, 71.15.Rf, 71.27.+a, 75.10.Lp

I. INTRODUCTION

During recent years great efforts both experimentally and theoretically have been dedicated to explore and possibly understand the intricacies of the electronic structure of plutonium metal. One of the key questions arises from the fact that the α and δ phase are so different in some of their properties while being separated by a rather modest influence of temperature. For example, the peculiarity that δ-Pu expands an extraordinary 25% relative to α-Pu is well known, but not well understood. This and other differences between the α and δ phases are believed to originate from the $5f$ electronic structure in plutonium, which consequently has received considerable attention.

Experimentally, refined techniques have evolved and been applied to measure α and δ plutonium with recently published results. These include, for instance, photoemission,[3] x-ray absorption[4] and electron energy loss,[5] magnetic susceptibility,[6] and heat capacity.[7] Of particular interest for this investigation are the studies by van der Laan, Moore, and others[5,8,9] in which they were able to quantify the relative strength of the spin-orbit interaction for several actinides. This was accomplished by measuring the branching ratio of core-valence transitions in electron energy-loss spectra (EELS), relating their results to angular-momentum coupling schemes.

On the theoretical side, plutonium metal was initially analyzed from first principles by rather rudimentary electronic-structure calculations within the DFT. Although these early attempts[10] relied upon less than accurate approximations for the electron correlations, the spatial geometry of the charge density and the electron potential, they provided important clues to the dominant role of the $5f$-band states in the chemical bonds. Later, essentially the same theory with improved approximations was able to correctly reproduce the monoclinic ground state of plutonium[11] and thereby confirming the usefulness of the approach. At the same time, it became very clear[11] that something was missing in the theory because the face-centered-cubic (fcc) δ phase could not be realistically modeled. In more recent calculations this notable failure extended to include also the β and γ phases of plutonium.[1]

The grave inaccuracies of the applied DFT for the expanded phases of plutonium have been a motivating factor for developing other models[12,13] particularly for the δ phase. Nevertheless, the usage of DFT appears to be reasonable for all phases of Pu when spin and orbital electron-correlation effects are included in the treatment.[2] Specifically, these calcu-

lations include spin polarization, orbital polarization, and spin-orbit coupling and predict substantial spin and orbital magnetic moments. There has been no experimental evidence of large ordered spin moments in Pu, but the theoretical approach apparently capture enough correct physics that acceptable energies[1,2,14] are obtained. This notable contradiction is very interesting and needs an explanation. By analyzing the orbital and spin moment components separately it is clear[15] that the total moment is very close to zero, due to a substantial cancellation between the two. If this is true, at least two conclusions are obvious. (i) The orbital correlations in terms of spin-orbit interaction and orbital polarization are important and should not be ignored for Pu. (ii) Only experiments designed to decouple the spin and orbital contributions are relevant for revealing the magnetic moments. As regards (ii), neutron-scattering experiments can in principal accomplish this separation at least if the moments are ordered in some fashion. Then the spin and orbital magnetic form factors can be decoupled because their respective magnetization density is not equal throughout the crystal. Statement (i) needs to be quantified further. How important are the orbital correlations relative to the spin correlations? This issue has not been addressed until now but is of significance because it may help illuminate the contradiction mentioned above.

Our report is organized as follows. Section II deals with some of the more important technical details regarding the calculations. In Sect. III we show results highlighting the relative importance of spin polarization, spin-orbit coupling, and orbital polarization. Finally, we offer a discussion in Sect. IV.

II. COMPUTATIONAL DETAILS

The electronic structure and total energy are obtained from two versions of the linear muffin-tin orbitals method (LMTO). A full potential (FP) version is used for calculating the equation-of-state for δ-Pu as well as the electronic density-of-states (DOS) applied for the analysis of the results. The more approximate application of the LMTO is within the atomic sphere approximation (ASA) which is here combined with the fixed-spin-moment method (FSM) that allows the spin moment to be constrained. This is particularly useful when investigating the influences the spin moment has on the orbital moment, total energy, and the electronic structure in general.

The FPLMTO implementation[16] has been used extensively and successfully for

transition[17] and actinide[18] metals. The "full potential" refers to the use of non-spherical contributions to the electron charge density and potential. This is accomplished by expanding these in cubic harmonics inside non-overlapping muffin-tin spheres and in a Fourier series in the interstitial region. We use two energy tails associated with each basis orbital and for the semi-core $6s$, $6p$, and valence $7s$, $7p$, $6d$, and $5f$ states, these pairs are different. Spherical harmonic expansions are carried out through $l_{max} = 8$ for the bases, potential, and charge density. For the electron exchange and correlation energy functional, the GGA[19] is adopted.

The LMTO-ASA[20] applies a spherical approximation to the electron charge density and potential and is therefore less suitable for open crystal geometries. Here, however, we are only considering the close-packed fcc (δ) phase of Pu. The present implementation of this technique includes the FSM which is of particular interest when investigating the effects of spin polarization. The FSM has been described[21] in the literature, but briefly it poses a boundary condition on the total spin moment in the calculation. This can be accomplished by defining a separate Fermi level for each spin band. By adjusting these levels a chosen total spin moment can be established for which the self-consistent total energy and other properties are evaluated. The electron exchange and correlation is parameterized as suggested by von Barth and Hedin[22] which appears to be a better choice[23] than the GGA for the ASA.

Integration over the irreducible wedge of the Brillouin zone is performed using about 500 or more k points to safely insure converged electronic structure for δ-Pu.

The spin-orbit coupling (SO) and orbital polarization (OP) schemes are implemented identically for both the FP and the ASA methods. The former is introduced in the customary fashion according to the suggestions by Andersen[24] for the $6d$ and $5f$ states, while omitted for the p states on the recommendation by Nordström *et al.*[25] The orbital polarization is accomplished as described before.[26] The orbitals with the spin, orbital, and magnetic quantum numbers (σ, l, m_l) are shifted an amount proportional to $L_\sigma m_l$. Here L_σ is the total orbital moment from electrons with spin σ. This self-consistent scheme attempts to generalize Hund's second rule for an atom to the condensed matter and enhances the separation of the m_l orbitals caused by the spin-orbit interaction. Hence, the OP can be viewed as an amplification of the SO and the total orbital moment. It is important to note that OP influences the electronic structure regardless of the spin polarization even though the total orbital moment, $L = \sum_\sigma L_\sigma$, will cancel for zero spin moment. This is a

consequential observation as we shall see below.

As the primary goal of this study is to quantify the importance of the spin versus orbital contributions we focus only on ferromagnetic spin order, although disorder or antiferromagnetic configurations have been suggested[1,27] for δ-Pu.

III. RESULTS

In Fig. 1 we show the FPLMTO total energies for four types of calculations. The highest (least favorable) energies are obtained from the non-magnetic (zero spin moment) treatment without spin-orbit coupling (NM: No SO). The minimum of this energy curve defines the zero level of the plot and occurs at an atomic volume of 17.9 Å^3, marked with a vertical dashed line. Hence, DFT on this level of approximation severely underestimates the atomic volume for δ-Pu, while equally seriously overestimate the bulk modulus, see Table I. It is also known from previous investigations that this treatment results in a negative tetragonal shear constant[30] and a DOS incompatible[31] with photoemission spectra.

Further in Fig. 1 we notice that the inclusion of spin-orbit coupling (NM: SO) lowers the total energy substantially and expand the equilibrium volume to a better, but far from acceptable, 19.9 Å^3. This is in complete agreement with electron energy-loss spectroscopy results that indeed show the spin-orbit interaction in plutonium is strong.[5,8,9,32] The bulk modulus is still too large compared to hand book data, see Table I.

By also allowing additional orbital correlations within the orbital polarization scheme (NM: SO+OP) the total energy drops further while significantly expanding the lattice to a more realistic equilibrium volume ($\sim$ 24 Å^3) as well as bulk modulus (Table I). The reason for this quite interesting improvement of the modeling of δ-Pu arises from the inclusion of orbital interactions that strongly perturb the electronic structure. The effect of SO and OP expands the lattice a great amount of almost 34% while lowering the total energy by more than 0.1 Ry/atom (1.36 eV/atom) and correcting the bulk modulus. Previous DFT investigations of δ-Pu have not clearly made this observation that *orbital correlations*, mainly of the $5f$ electrons, are very important for the bonding characteristics in δ-Pu while the effect of ferromagnetic spin polarization (FM: SO+OP), see Fig. 1, is much less pronounced. As we shall see below, however, the reason for this confusion lies in the fact that when these orbital correlations are neglected, the spin polarization increases and compensates for the

missing interactions.

Next, in Fig. 2, we present fixed-spin-moment LMTO-ASA calculations for δ-Pu performed for the experimental lattice constant (4.64 Å). The total energies are all shifted so that the non-magnetic (spin equals zero, "No SO") result defines the zero energy.

Focusing first on the energies (blue) from the treatment without SO, we notice two important facts. First, spin polarization is very important within this approximation with an energy gain of more than 0.04 Ry/atom associated with the formation of ferromagnetically ordered (5 μ_B) spins. Second, the total energy is always *higher*, regardless of spin moment, compared to the SO (red) and the SO+OP (black) models. These two statements conclude that a spin-polarized only (no SO) theory is missing some essential orbital correlations for which the spin polarization alone can not fully compensate.

The red curve in Fig. 2 refers to calculations that include spin-orbit coupling (SO). Clearly this mechanism plays a dominant role in the total energy and lowers it by about 0.08 Ry/atom when the spin moment is fixed to zero. Allowing ferromagnetism (non-zero spin moments) only lowers the total energy slightly further. As mentioned, a non-magnetic treatment on this level of approximation is clearly favorable over any ferromagnetic calculation without SO, suggesting spin-orbit is stronger than electron exchange interaction in Pu, and this has indeed clearly been shown.[9]

The best model, from a total-energy standpoint, includes spin-orbit coupling and orbital polarization (SO+OP). The OP mechanism provides for another $\sim$ 0.02 Ry total-energy gain in addition to that from the spin-orbit coupling. As in the case of the SO (no OP) theory, the formation of ordered spin moments influences the total energy only a slight amount. Notice also that the calculated spin moments reduce substantially when SO and OP are included, from about 5 to 3.5 μ_B. Hence, without the orbital contributions the spin moment is greatly amplified. In our variational theory the search for the lowest energy (ground) state is accomplished by varying all degrees of freedom and the exaggerated spin moments are simply compensating for the missing physics related to orbital correlations.

When analyzing the importance of spin polarization on one hand and the orbital contributions in terms of SO and OP on the other, Fig. 2 is particularly relevant. We conclude from the plot, and the SO+OP treatment (black), that the total-energy gain associated with these orbital effects is about 0.11 Ry for a non-magnetic (zero spin) model. The additional energy contribution arising from the formation of ferromagnetic spin moments is $\sim$ 0.01 Ry

or about 8% of the total gain. In other words, the orbital correlations (92%) are of dominant importance for the total energy compared to the spin correlation (8%) in δ-Pu.

If spin polarization is of less importance in the full theory, as the energetics in Fig. 2 suggests, the electronic structure and DOS should not be greatly modified when spin polarized. In Fig. 3 we show the DOS for the SO+OP model for fixed zero (NM: SO+OP) and optimized (3.5 μ_B) ferromagnetic spin moment (FM: SO+OP). The former DOS is shifted up an amount of 2.5 states/eV for a clearer display of the results. The first four peaks below the Fermi level (E_F at zero energy) in the DOS are marked A-D. All peak-locations compare closely to each other for the NM and FM configurations with the largest discrepancy being a shift of about 0.07 eV. Both DOSs have a peak close below the E_F, with the magnetic (FM) peak (A) being somewhat closer (-0.10 eV), which is consistent with the known photoemission spectra of δ-Pu.[3] Hence, the process of spin polarization does not modify the quantitative behavior of the DOS, although on a detailed level there are some minor changes, particularly in peak intensities.

IV. DISCUSSION

We have shown that orbital correlations such as spin-orbit coupling and orbital polarization, which essentially enhances the effect of the spin-orbit coupling, are very important for δ-Pu. It is also clear that electron-orbital correlations dominate over electron-spin polarization in this case. Interestingly, recent EELS measurements[8,9] nicely confirm that for plutonium the spin-orbit interaction dominates over exchange (spin) interaction. Moore *et al.*[9] also discovered that for curium, one of plutonium's heavier neighbors, there is a shift from optimal spin-orbit stabilization to optimal exchange interaction stabilization. For our Pu electronic-structure model to be realistic, it must be agree with the transition in emphasis, spin-orbit towards exchange interaction, that obviously occurs for Cm.[9]

In Fig. 4 we display results similar to those shown in Fig. 2, focusing only on the full treatment including spin-orbit coupling and orbital polarization, for δ-Pu (black) and Cm (red). Both curves are shifted to zero energy for fixed zero spin moment. To make the comparison as consistent as possible, we chose the fcc phase (Cm-II) of curium which serves as a good representative of the close-packed hexagonal ground state.[9] As noted above, the spin-polarization energy for δ-Pu in Fig. 4 is rather modest while for Cm the opposite is

true. In fact, the spin-polarization energy for Cm is about one order of magnitude larger than that for Pu (0.11/0.012 = 9.2). The contrasting behavior shown by Pu and Cm in Fig. 4 directly supports the transition in the $5f$-electron coupling towards dominance of the exchange interaction found for Cm in the recent EELS measurements.[9]

To conclude, we have quantified the importance of spin magnetic moments in δ-Pu within the DFT and shown that although the model predicts spin magnetic moments they are shown to be relatively unimportant when spin-orbit coupling and orbital polarization are included in the theory. We have further shown that the spin moments are not necessary for a reasonable lattice constant in δ-Pu and that the key features of the electronic density-of-states do not depend sensitively on the spin polarization. Lastly, we have shown that the DFT model is able to distinguish Cm from Pu, in the context of quantifying the balance between spin-orbit and exchange interaction, in a manner completely consistent with EELS measurements and their interpretations.[8,9]

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Figures

FIG. 1: Results from FPLMTO total-energy calculations of δ-Pu. The non-magnetic treatments (NM) refer to calculations with no spin moment, and are presented for three levels of approximation. No spin-orbit coupling (NM: No SO), with spin-orbit coupling (NM: SO), and (NM: SO+OP) also adds orbital polarization. The (FM: SO+OP) theory is identical to the (NM: SO+OP) with the exception of allowing for ferromagnetic spin order. Their respective equilibrium volumes are marked with a dashed vertical line and the 593 K atomic volume of δ-Pu is marked as (V_δ).

FIG. 2: (Color online). Results from LMTO-ASA total-energy calculations of δ-Pu as a function of fixed spin moment, utilizing the fixed-spin-moment method. The blue (No SO) curve corresponds to calculations without spin-orbit coupling. The red (SO) includes spin-orbit interaction and the black (SO+OP) also adds orbital polarization. The calculations are performed for a fixed atomic volume, 25 Å^3, corresponding to the 593 K lattice constant of δ-Pu (4.64 Å).

FIG. 3: FPLMTO total DOS for SO+OP calculations with no (NM: SO+OP) and ferromagnetic (FM: SO+OP) spin configurations. The former is shifted an amount of 2.5 states/eV to enable a clearer display of the results. The location of the peaks A, B, C, and D, compares well between the two models.

FIG. 4: (Color online). Results from LMTO-ASA total-energy calculations of δ-Pu (black) and fcc curium (red). The curves are shifted to zero energy for fixed zero spin moment. The calculations are performed for fixed atomic volumes corresponding to the experimental lattice constant for δ-Pu (4.64 Å) and Cm (4.93 Å). The electronic structure include spin-orbit coupling and orbital polarization.

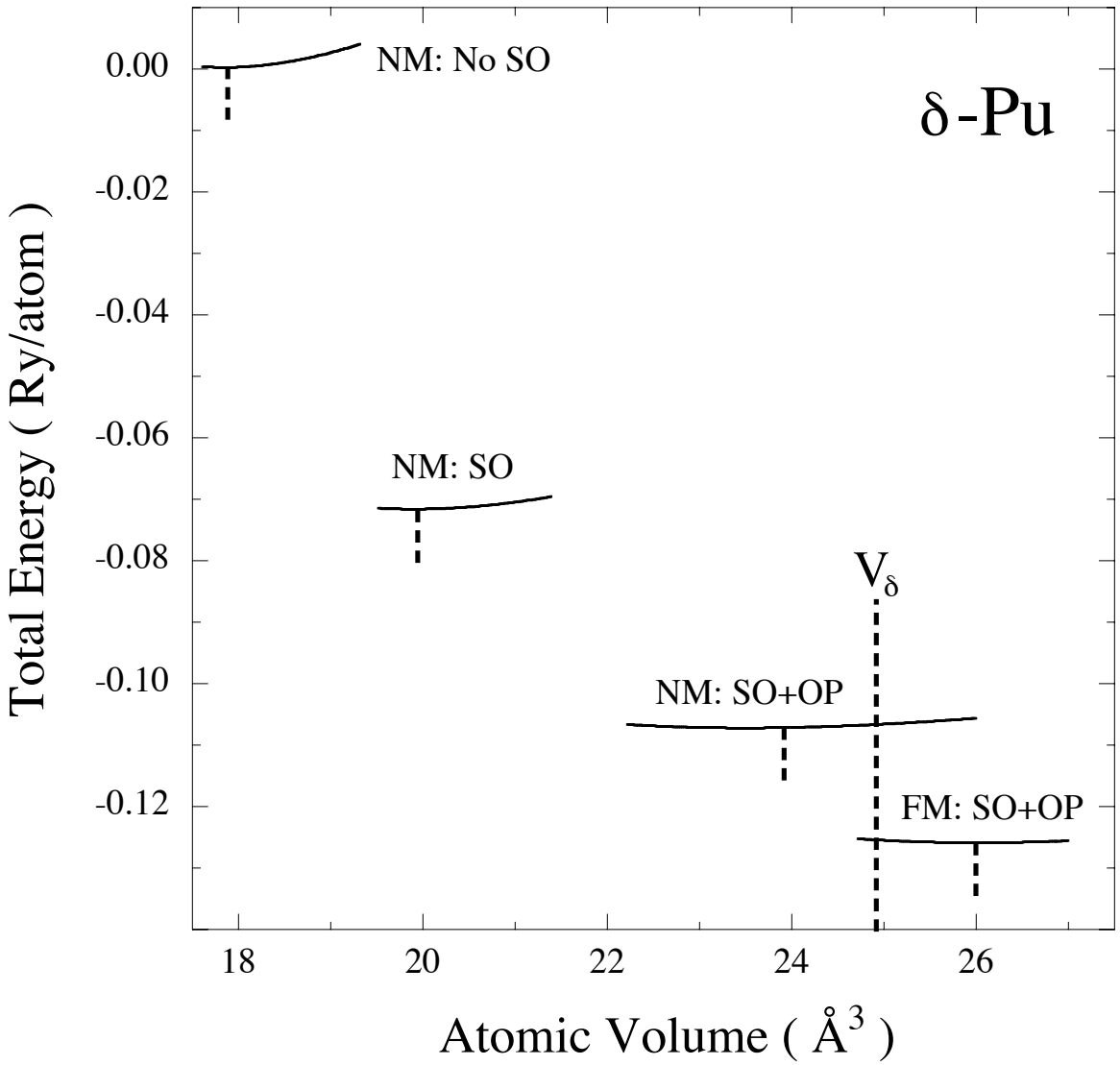
Tables

TABLE I: Equation-of-state data for δ-Pu corresponding to the FPLMTO total energies shown in Fig. 1. An explanation of the theoretical models is given in the main text. The equilibrium volume, V, and bulk modulus, B, are given in units of Å^3 and kbar, respectively.

Model	V (Å^3)	B (kbar)
NM: No SO	17.85	1600
NM: SO	19.90	900
NM: SO+OP	23.94	480
FM: SO+OP	26.00	400
Experiment	25.0[a,b]	300[a], 290[b]

[a] Ledbetter and Moment[28]

[b] J. Wong *et al.*[29]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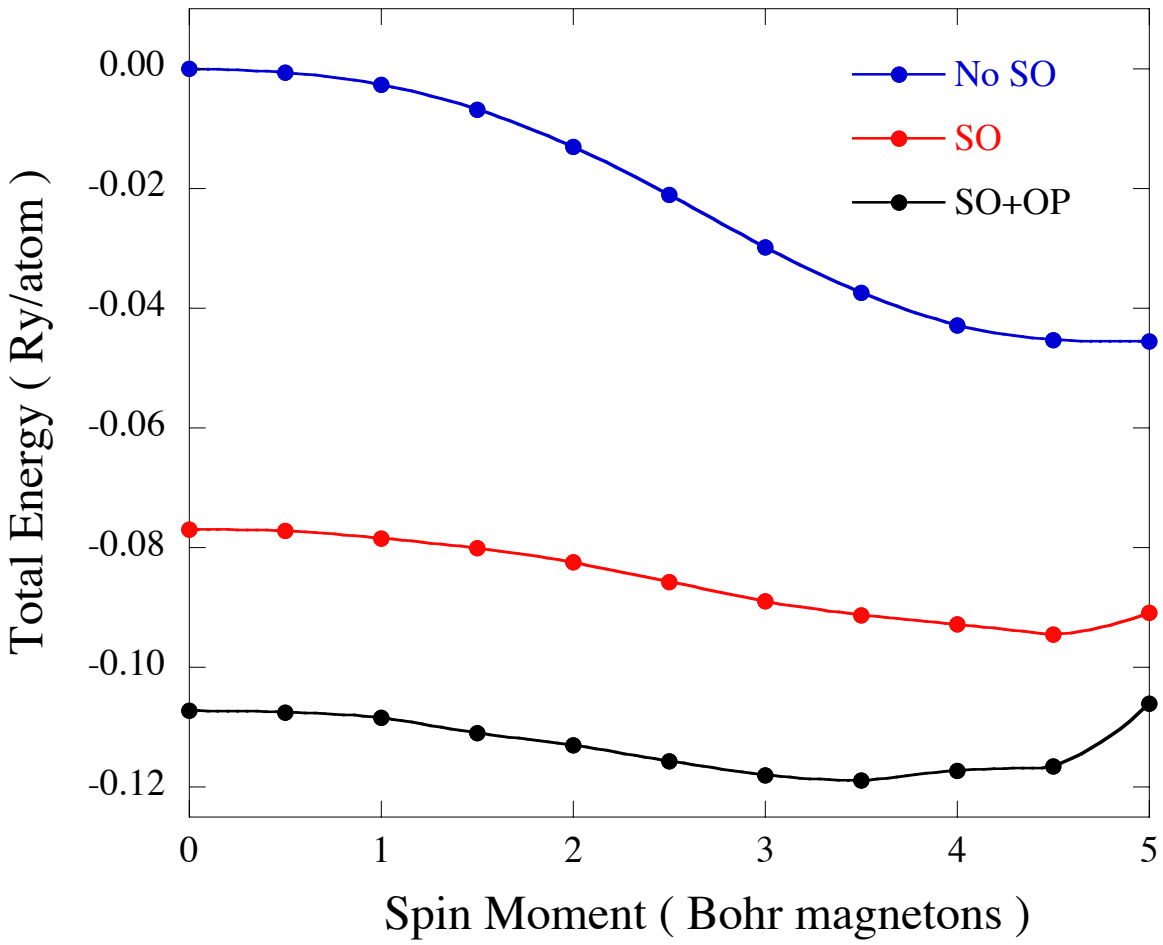
-0.06
-0.08
-0.10
-0.12
Total Energy (Ry/atom)
NM: No SO
δ-Pu
NM: SO
V$_\delta$
NM: SO+OP
FM: SO+OP
18
20
22
24
26
Atomic Volume (Å^3)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-0.04
-0.06
-0.08
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-0.12
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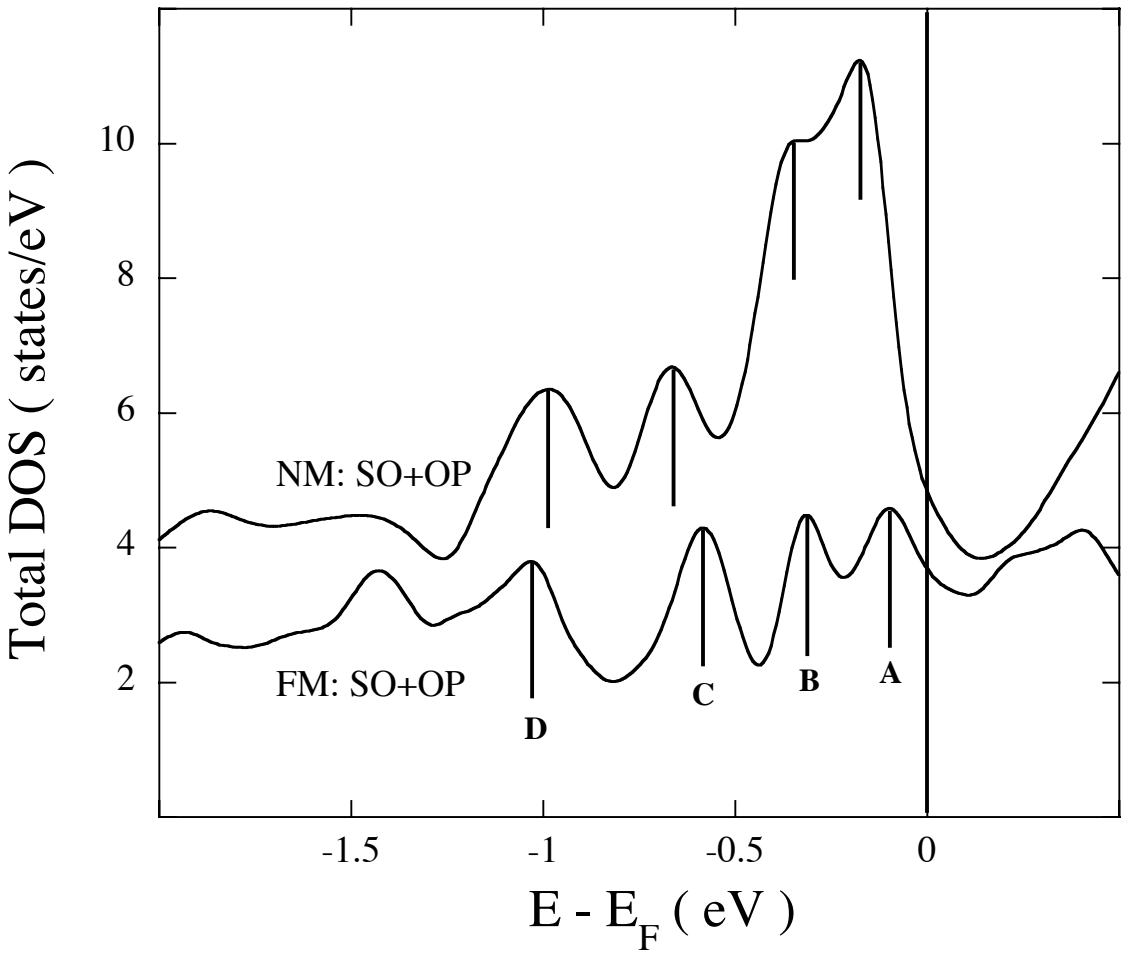
2
3
4
5
Spin Moment (Bohr magnetons)
No SO
SO
SO+OP


Total DOS (states/eV)
10
8
6
4
2
NM: SO+OP
FM: SO+OP
D
C
B
A
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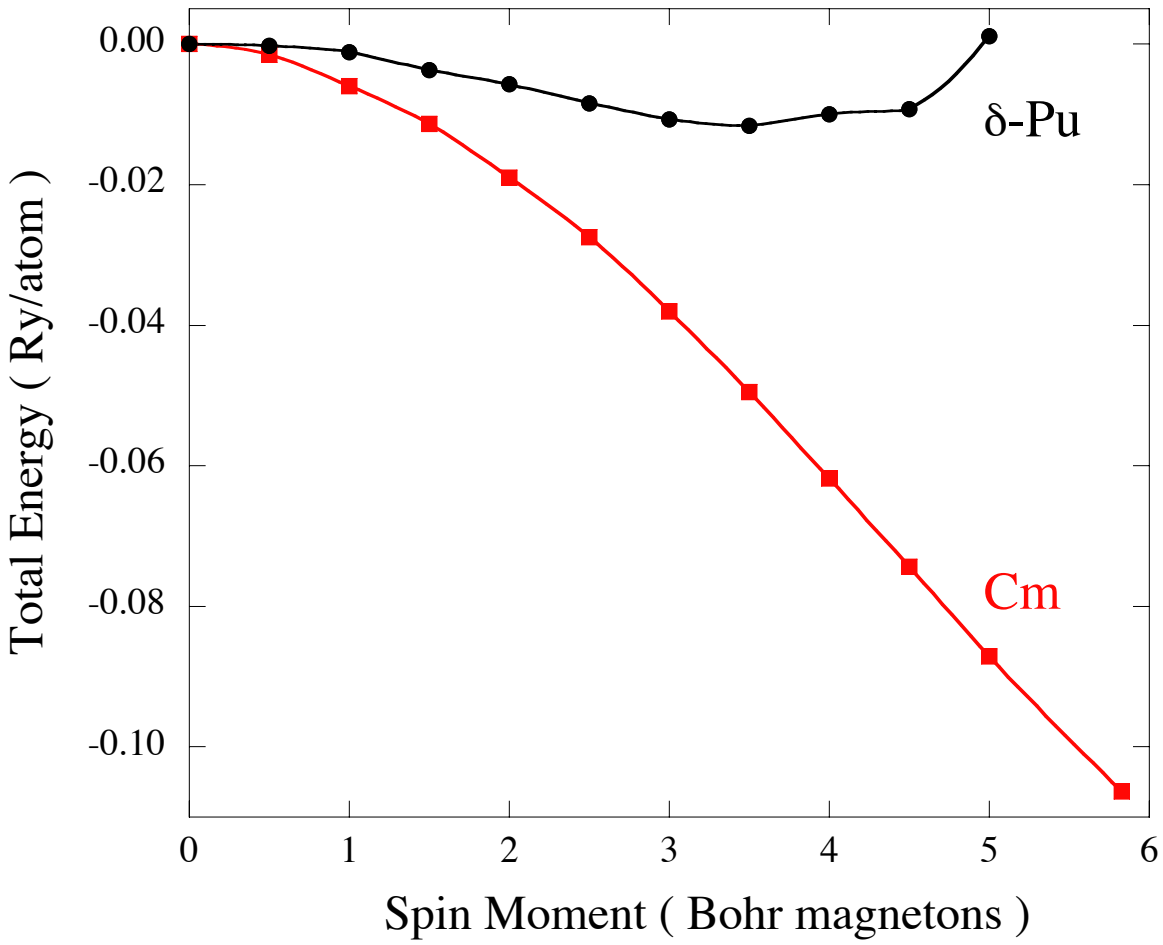
-1
-0.5
0
E - E_F (eV)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-0.02
-0.04
-0.06
-0.08
-0.10
Total Energy (Ry/atom)
0
1
2
3
4
5
6
Spin Moment (Bohr magnetons)
δ-Pu
Cm